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*The Effects of Moisture on the Dynamic
Mechanical Properties of Ammonium
Perchlorate — Polyurethane Propellants*

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A handwritten signature in cursive script, reading "Robert F. Landel", written over a horizontal line.

R. F. Landel, Chief
Polymer Chemistry Section

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ABSTRACT

The detrimental effect of moisture on ammonium perchlorate-polyurethane propellant appears to be due to one or more of the following mechanisms: solution, migration and precipitation of the oxidizer. Direct microscopic observation indicates that the ammonium perchlorate grains are physically separated from the binder, when exposed to relative humidities greater than 15% at ambient temperatures. This physical dewetting leads to small-strain dynamic shear compliance instability which is a function of time and environment. The environmental effect, producing either a softening or an embrittlement, is established to be a function of the previous humidity history and the environment at the time of measurement. There appears to be an optimum amount of water necessary for maximum embrittlement at any given temperature, and additional water tends to decrease embrittlement. The detrimental effects can be reversed, apparently by a healing of the salt-binder adhesion on the surface of the initial grains, and additional reinforcement provided by the precipitation of new, euhedral crystals of ammonium perchlorate.

I. INTRODUCTION

Earlier studies (Ref. 1, 2, and 3) have determined that there is a relationship between the water content of a filled polyurethane system and the mechanical properties displayed by that system. It was shown that the tensile strength (σ) and percent elongation (ϵ) decrease rapidly when samples are exposed to relative humidities greater than 15% at 26° C. At 10 to 15% RH, the properties remain more or less stable (ϵ) or decrease slowly (σ), and at 2% there is a slight improvement (Fig. 1). These values correlate very well with moisture adsorption isotherms (Fig. 2) plotted using data from Ref. 1 and 2. In other words, at 26°C, it appears that a change in propellant tensile strength and elongation, whether increasing, decreasing, or remaining stable, is a direct function of whether the propellant is adsorbing water, desorbing water, or is at equilibrium with its environment, respectively. However, as was shown by embrittlement studies (Ref. 3) of Aerojet-General Corp. and by measurements of dynamic mechanical properties made during the course of this work, this generality does not hold true at lower temperatures.

Aerojet has found that storage of samples at low temperatures, after equilibrium at room temperature and 80% RH, caused large increase in tensile modulus and de-

creases in elongation at maximum load; this phenomenon was called embrittlement. They found that the degree of embrittlement depended on the initial moisture content of the sample and upon the type of filler used. For example, between the temperatures -60°C and 24°C, there was an increasingly sharp rise in degree of embrittlement with the fillers potassium perchlorate, ammonium perchlorate, and lithium perchlorate. Ammonium sulphate, aluminum, glass beads and potassium chloride fillers did not initiate embrittlement.

Studies on the effects of moisture were resumed at JPL because of their importance to studies on the dynamic mechanical properties of a polyurethane propellant. The dynamic loss modulus was especially desired because of its importance to combustion instability studies (Ref. 4), but a unique difficulty was encountered in making the measurements, which ultimately led to the other experiments discussed. The major effort consisted of direct microscopic observations of the behavior of small amounts of lithium perchlorate, ammonium perchlorate, ammonium sulphate, and glass beads dispersed in a binder and exposed to various relative humidities. In addition, the results of qualitative electrical measurements, attempts to measure the diffusion constant of water, and infrared spectral analysis are also repeated herein.

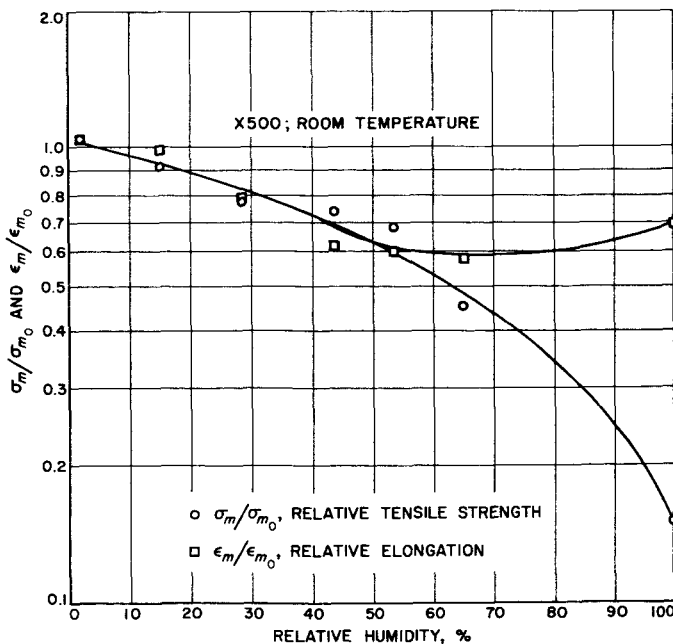


Fig. 1. Propellant tensile properties, after reaching equilibrium moisture content, as a function of relative humidity

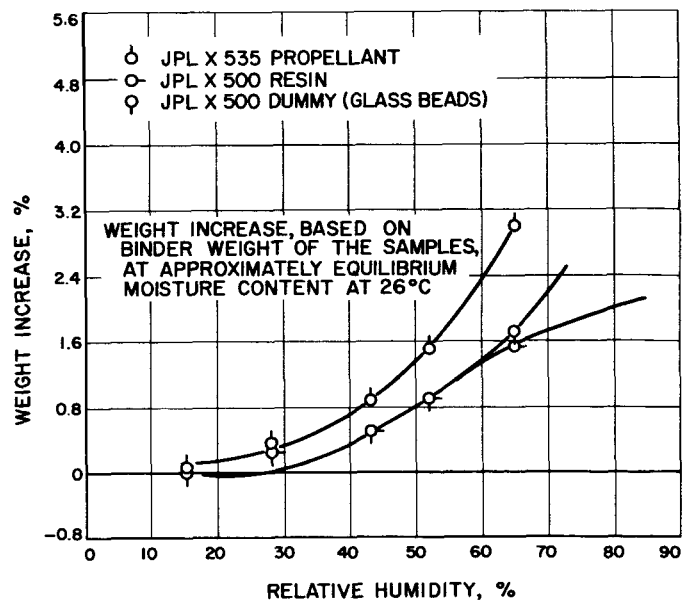


Fig. 2. Adsorption isotherms for three systems

II. DYNAMIC MECHANICAL PROPERTIES

Measurements of the dynamic mechanical properties of a polyurethane-ammonium perchlorate propellant, using the Fitzgerald transducer apparatus, were performed over a wide temperature and humidity range. The Fitzgerald apparatus is a device capable of measuring the dynamic shear compliance over the frequency, temperature, and compliance (reciprocal modulus) ranges of 30 to 6,000 cps, -50 to 150°C , and $10^{-10.5}$ to 10^{-6} cm^2/dyne , respectively. The normal procedure followed in taking data is to measure the properties at several frequencies for one temperature, repeat the measurement for progressively lower temperatures, and finally rerun some of the higher temperatures to check the results initially obtained. Ordinarily the results are in good agreement, but propellant samples have always proven to be unstable and check runs have seldom agreed with the original runs¹. Studies of a model filled system of glass beads in polyisobutylene (Ref. 5) have indicated that the instability is not associated with the filler per se.

It was believed that in the present experiments the use of propellant samples prepared under more exacting conditions² and a stricter control of humidity (dewpoint of about -60°C instead of -30 to -40°C) would remove the main sources of the instability. However, this did not prove to be the case. Sample properties could not be reproduced except at room temperature (22°C). Since completing this portion of the work, Atlantic Research Corp. has also encountered this poor reproducibility even with different binder systems. (Ref. 6).

A. Low Humidity Experiments (-60°C Dewpoint)

In searching for the origin of the poor reproducibility, it was found that the modulus increased with time (compliance decreased), and so attention was turned from the absolute magnitude of the compliance to the drift itself. Figure 3 shows some of the results from a set of samples which had been in the apparatus some 4 months. Results from a prior set of samples (of different dimensions) cut from the same block of propellant³ were very similar in both the absolute magnitude of the compliance and the drift rate. Therefore, the observed drift is reproducible.

¹R. F. Landel, unpublished results.

²Studies by E. Cuddihy, A. J. Havlik, and J. Moacanin on the homogeneity of polyurethane propellants, (to be published).

³The block had been stored at room temperature over Drierite.

Initially it was thought that the effect was due to a lag in establishing equilibrium. This is often the case in crystallizing systems and in gels, where the final properties are strongly dependent on the previous thermal history. Indeed a slight drift toward decreasing compliance (increasing modulus) was noted, although generally the amount of change from day-to-day was so small that it was barely detectable even with the great sensitivity of the apparatus.

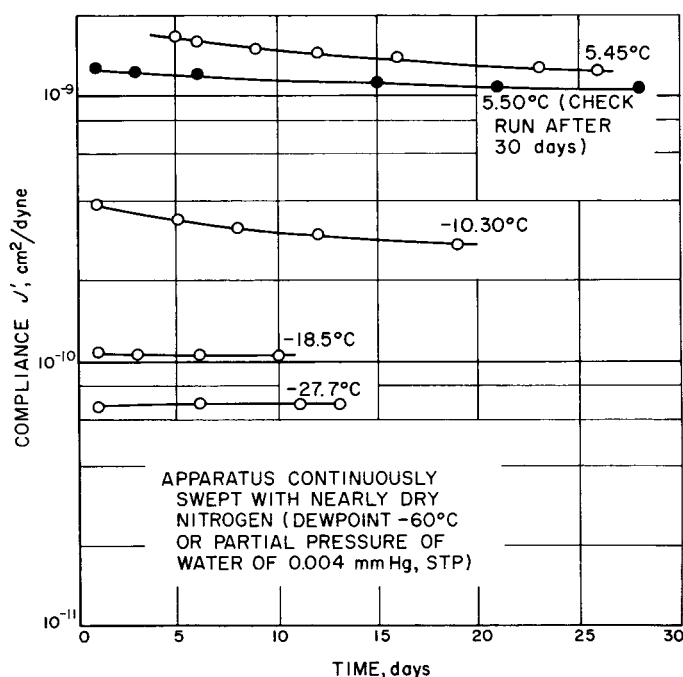


Fig. 3. Drift in shear storage compliance at 800 cps for an X500 polyurethane-ammonium perchlorate propellant

Therefore various temperatures between $+22$ and -20°C were approached both from above and from below. If the drift were simply a slow attainment of equilibrium, an approach from a lower temperature should result in a drift upward with time, toward the same asymptotic value indicated in the downward drift. The results were negative. There was no asymptotic value and the compliance always drifted downward if it showed any change at all. This was illustrated by the check run at 5.5°C , taken after the sample had been at various low temperatures.

The properties were found to be stable at 22 and -28°C and to have a maximum drift rate of about 3% per day at -10°C . However, although this drift rate proved to be independent of previous thermal history, it did not prove to be independent of previous relative humidity history.

B. Variable Humidity Experiments

A precise method of moisture control of a nitrogen atmosphere was devised. Dry nitrogen is passed through a water bath to a series of traps in an air thermostat and then into the apparatus. The thermostat can be closely controlled for any desired temperature from -75°C to room temperature, or above. The excess water condenses in the traps of the thermostat, and these maintain the equilibrium vapor pressure of water in the gas stream entering the apparatus.

In the prior isothermal (26°C) studies on humidity, the change in properties of propellant was found to be reversible, to correlate with the amount of moisture absorbed, and to depend on whether or not the sample was in equilibrium with its environment (Ref. 1 and 2). The current experiments in the Fitzgerald apparatus verified the previous results, but with one very important qualification: at temperatures lower than about 24°C , a mechanism other than simple hydration-dehydration comes into action.

Figure 4a is a plot of compliance J' at two frequencies, 1200 and 800 cps, versus time at a constant temperature of 22.5°C , and with variable humidity. Initially the sample was at equilibrium in a nitrogen atmosphere in which the partial pressure of water was 0.004 mm Hg. When the partial pressure of water was increased to 1.9 mm Hg, the compliance abruptly increased (modulus decreased) in 1 day, though the abruptness is not apparent in the scale of the Figure. The compliance then drifted slowly upward for the succeeding 5 days. The partial pressure of water was then increased to 6.4 mm Hg. Again, there was an abrupt increase in magnitude and a succeeding leveling off. Next the partial pressure was lowered to 0.07 mm Hg and finally to 0.002 mm Hg. The effect of these two final values of partial pressure was the complete reversal of the modulus from drift downward to a drift upward. Apparently the sample was responding to changes in the partial pressure of water in its atmosphere

in the same manner as had been reported in previous studies. The modulus decreased (compliance increased) upon absorbing water and increased upon subsequent drying.

However, at lower temperatures, the mechanism of embrittlement came into play with such vigor that at 5°C an increase in partial pressure from 0.002 to 4.8 mm Hg resulted not in a decrease in the modulus, but in an increase of almost 100% in 4 days. This is illustrated by the storage compliance J' , Fig. 4b. (Figure 4c, the loss compliance J'' is included for completeness, but since its behaviour parallels that of J' , only the latter will be discussed.) Furthermore, decreasing the partial pressure to 0.48 mm Hg resulted not in a reversal of embrittlement, but in an immediate additional increase in the rate, with an eventual leveling off to equilibrium. An additional decrease in partial pressure to 0.03 mm Hg, held for 1 day, resulted in disruption of the equilibrium and further driving of the modulus upward (compliance downward). Finally the sample environment was returned to a water pressure of 4.8 mm Hg, a value that had previously produced a drastic increase in modulus. The result was now an equally drastic decrease in modulus.

This behavior can be explained if it is assumed that three mechanisms are operative to produce a change either upwards or downwards in a sample modulus:

Increase	Decrease
Sample dehydration Embrittlement	Sample hydration

It appears that at a given temperature there must be an optimum amount of water present to produce embrittlement; additional water merely reverses the trend and causes a modulus decrease due to hydration, with consequent dewetting of adhesive bonds. The data presented in Fig. 4a and b and additional data collected at -10°C (Fig. 4d) strongly support this argument. Additional support was provided by returning the sample to 23.5°C and a partial pressure of 0.09 mm Hg (Fig. 4a). The modulus, previously rather stable at that temperature, now drifted down rapidly. This downward drift indicated that the direction of drift and the absolute value of modulus is a function of both the sample humidity history and the sample environment at the time of measurement, and only indirectly a function of previous thermal history.

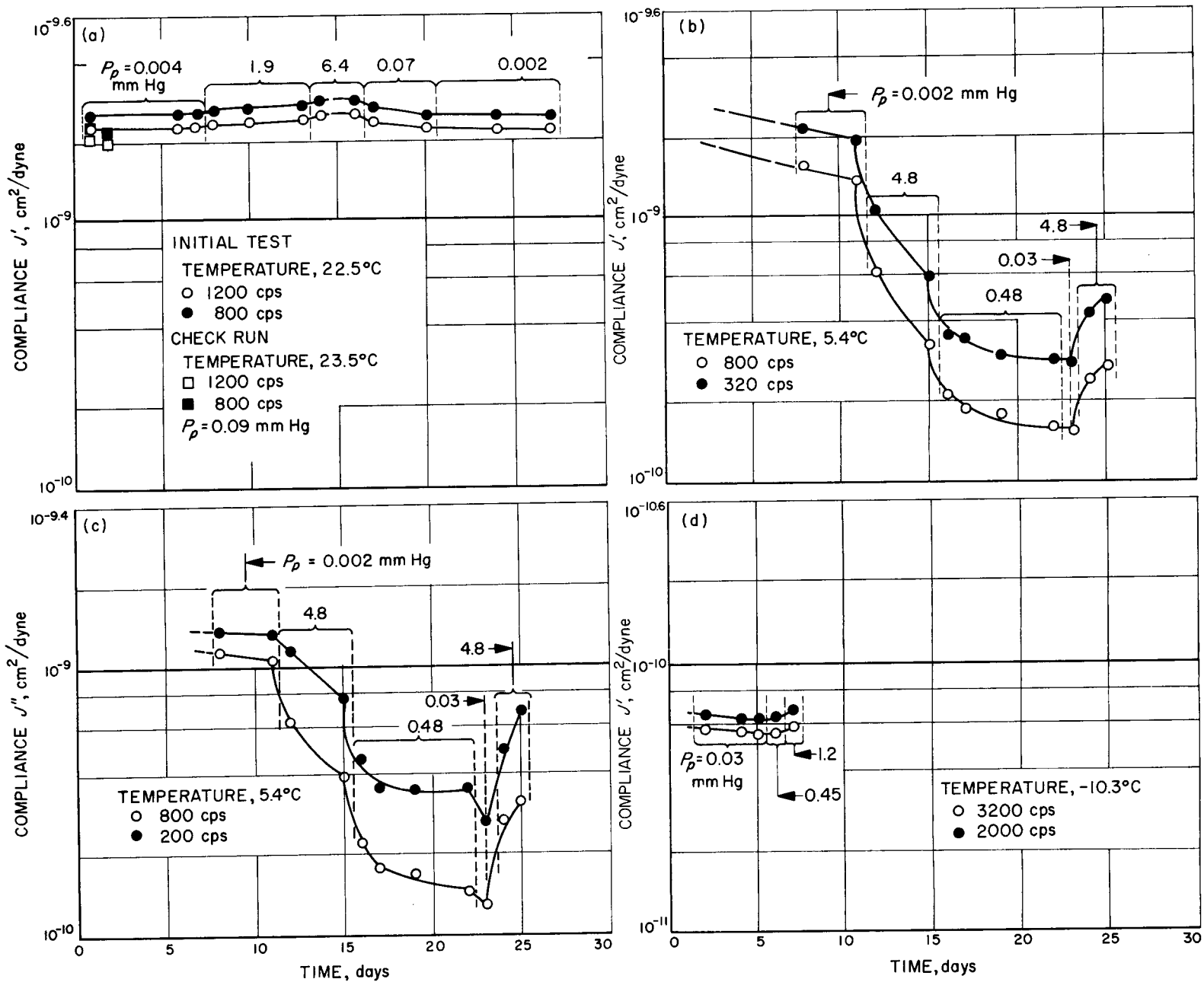


Fig. 4. Dependence of the dynamic shear compliance of a polyurethane-ammonium perchlorate propellant on the partial pressure of H_2O in the nitrogen atmosphere

III. MICROSCOPIC STUDIES

A. Experimental

Direct visual observation of the changes that take place at the surface of filler particles was accomplished by preparing samples of binder in which less than 1% of the filler was incorporated. The binder was then cast and cured between microscope slides held in a specially designed mold which resulted in sample dimensions of approximately $2.5 \times 7.5 \times 0.63$ cm. Table 1 gives the compositions of the propellant and binder used in the experiments. After curing the binder, samples were exposed to 0, 29, 76, and 100% RH. Relative humidities of 0 and 100% were obtained with P_2O_5 and distilled water; relative humidities of 29 and 76% were obtained with saturated solutions of $CaCl_2 \cdot 6H_2O$ and NaCl respectively (Ref. 1 and 2). The fillers used were lithium perchlorate, ammonium perchlorate, ammonium sulfate, and glass beads.

Table 1. Composition of binder for lightly filled systems

Binder	Composition
Polyoxypropylene glycol (POPG)	$NCO/OH = 1.06$ $OH \text{ triol/total } OH = 0.130$
Toluene diisocyanate (TDI)	
Trimethylolpropane (TMP)	
Ferric acetylacetonate (FeAA)	0.03 wt %

Corollary experiments were made in which the filler particles were observed in the dry state, under acetone or benzene, after the volatile solvent had evaporated, and under PPG.

B. Results: Liquid Immersants

The dry crystalline materials had a rough, pitted surface which resulted in a mottled appearance under the microscope, as exemplified by an ammonium perchlorate crystal in Fig. 5a. Figure 5a illustrates the rough surface structure of dry crystals; Fig. 5b, the glassy, undifferentiated surface of crystals immersed in a liquid or as they initially appear in a cured binder. The dry crystals display much surface relief such as pits and fractures. When



Fig. 5. Ammonium perchlorate crystals: (a) Dry; (b) In a polyurethane binder

wetted by a liquid, the topography of the salt crystal and the imperfections of glass beads disappear and all surfaces appear smooth and glassy. After the volatile solvents evaporate, the initial rough appearance is restored, showing the degree of smoothness to be related to the degree of wetting. This change in appearance really depends on the refractive index difference between the crystals and the liquid. However, in these qualitative observations, there was little difference in the appearance of the crystals over the range of refractive indices covered (Table 2).

Table 2. Refractive indices of crystals and immersion fluids

Material	n_D^{25}
Ammonium perchlorate	1.4833
Ammonium sulfate	1.521–1.533
Lithium perchlorate	—
Acetone	1.3591
Benzene	1.5016
PPG 2025	1.4494

C. Results: Binder

The fillers in the cured binder initially had the same appearance as when immersed in the liquids—smooth and glassy. There was no change with time for any of the samples stored at 0% RH. Neither was there any change in the appearance of the glass bead surfaces stored 21 days at 100% RH. However, the appearance of the salts changed progressively with time, the lithium perchlorate being most rapidly and severely affected.

1. Lithium Perchlorate

Figure 6a shows a lithium perchlorate crystal in the cured binder after being subjected to 100% RH at 23°C for 24 hours. Small whiskers of lithium perchlorate can be seen growing from the surface of the initial crystal. The same crystal is shown 7 days later in Fig. 6b. The needle-like crystals have now become fuzzy and indistinct, and hundreds of tiny dots or circles appear in the binder at relatively large distances from the initial grain. These dots apparently represent lithium perchlorate which dissolved in the binder, migrated away from the initial crystal, and then precipitated. They begin to be observable on the second day, and form a halo which increases in diameter with the passage of time. Ultimately, the lithium perchlorate grain disappears completely and the original space becomes occupied by a cloud of thousands of these small crystals. Drying the sample over P_2O_5 (0% RH) for 2 weeks did not change this appearance.

2. Ammonium Perchlorate

Because the binder adhered to the microscope slides, and moisture could penetrate only from the edges, it was possible to observe progressive changes in the appearance of the filler surface and to record rates of these qualitative changes. Figure 7 shows the rate at which

complete dewetting of the ammonium perchlorate grains proceeded into the interior of the microscope slides at 100, 76 and 29% RH.

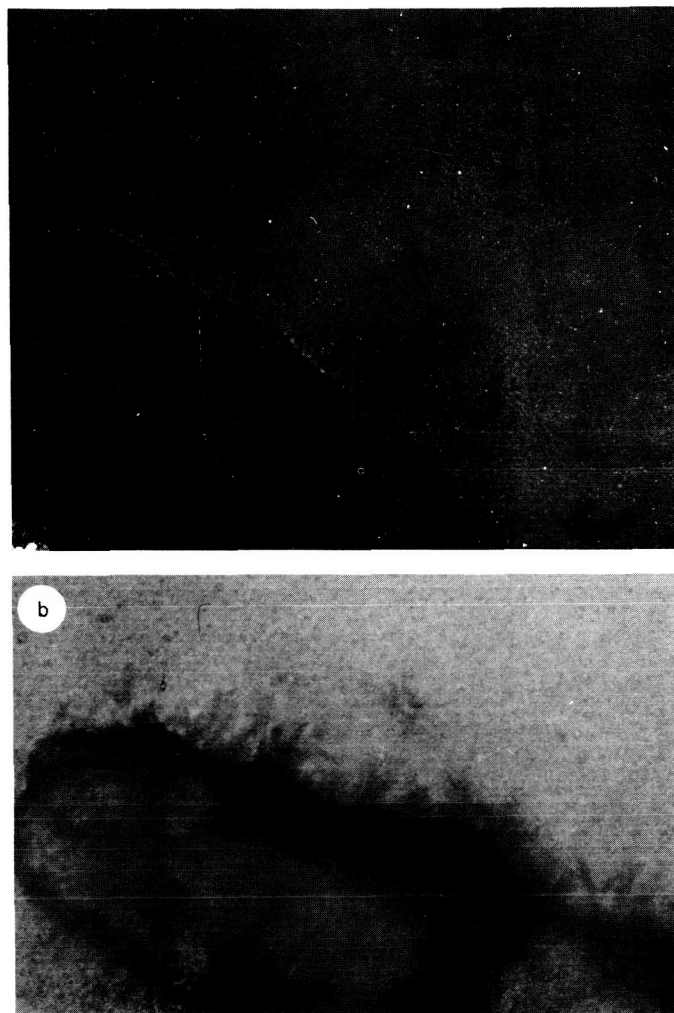


Fig. 6. Lithium perchlorate crystal in a cured polyurethane binder after exposure to 100% RH at 23°C: (a) After 24 hours, showing recrystallization; (b) Same crystal after 8 days

Figure 8 is a photomicrograph that illustrates the three stages of adhesion or wetting. The smooth area is complete wetting (complete adhesion); the rough pitted area is partially dewetted (many of the adhesive bonds between filler grain and binder chain have been completely destroyed). The dark, opaque area indicates that all bonds have been destroyed and the grain is surrounded by a vacuole. This vacuole formation is defined as complete dewetting and can be followed easily by observing the crystals between crossed polaroids on a petrographic

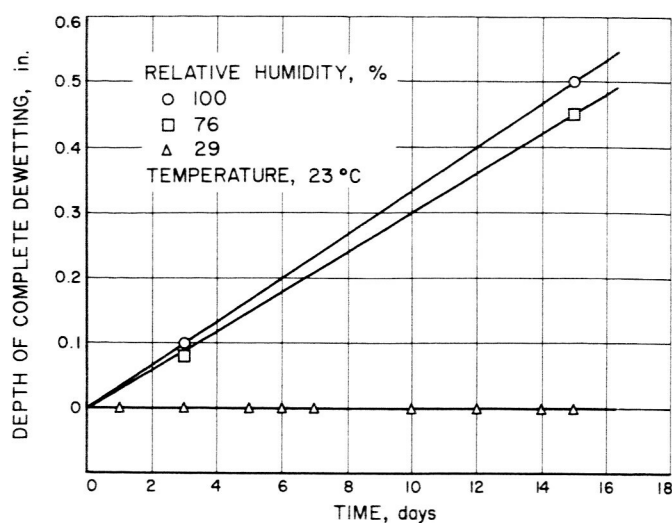


Fig. 7. Rate of complete physical dewetting of ammonium perchlorate grains from JPL X500 binder in approximately 1/2 % loaded system

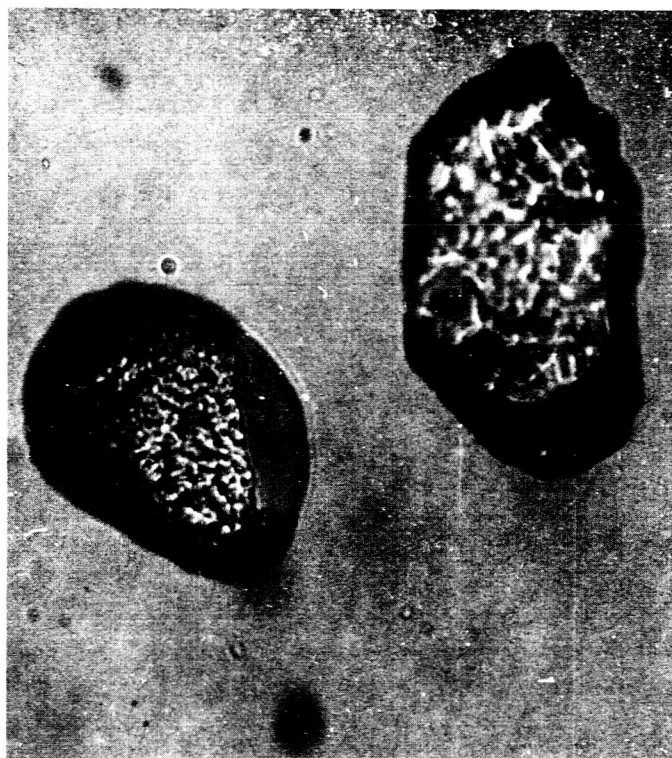


Fig. 8. Three degrees of dewetting of ammonium perchlorate crystals

microscope. The smooth, wetted crystals and the partially dewetted crystals always transmit some light because they are weakly birefringent and depolarize the trans-

mitted light. When a vacuole forms, however, the crystal appears opaque and remains extinguished at all angles throughout the rotation of the microscope stage. This is probably due to total reflection around the vacuole, since small bubbles in the resin give the same effect.

When samples that have been dewetted at 100, 76 or 29% RH are dried over P_2O_5 for up to 28 days, the oxidizer particles continue to present an opaque, extinguished appearance; in other words, there is no rehealing of the destroyed adhesion. This is not in agreement with stress-strain data previously obtained (Ref. 1 and 2). These data showed that after subjecting samples to various relative humidities and subsequent drying, the original properties were largely restored, with the exception of 100% RH where ϵ_m was increased. Because very little optical dewetting took place after 30 days at 29% RH, but rather large differences in the tensile behavior of the propellant were measured, it logically follows that there are changes in the mechanical properties before enough dewetting has occurred to make it optically apparent. Furthermore, judging from the stress-strain data of Ref. 1 and 2, these invisible changes that appear before optical dewetting are reversible under normal conditions.

However, the complete dewetting that is optically observable is reversible under somewhat abnormal drying conditions. A slide containing completely dewetted ammonium perchlorate grains that had failed to heal after 28 days over P_2O_5 was exposed for 36 hr at 72°C and a vacuum of 20 mm Hg. Not only did complete rehealing take place, but precipitation of many euhedral crystals occurred throughout the binder (Fig. 9). (The euhedral crystals are the small rectangular ones.) Some of the initial crystals can be seen, though slightly out of focus, and their smooth, glassy surface is apparent. Due to the thickness of the microscopic slides, it was impossible to employ the high power objective lens necessary for quantitative crystallographic identification, but the new euhedral crystals were qualitatively compared with the rehealed grains and found to be ammonium perchlorate. Clearly, the ammonium perchlorate went into solution at the salt-binder interface during dewetting and migrated into the binder. Whether the solvent is the interstitial water or the binder is not known at this time; however, Table 3 presents the solubility of various fillers in POPG. Significantly, the order of solubility of the salts is the same as the order of intensity of embrittlement as reported by Aerojet. As noted in Table 3, only the KC1-POPG mixture was tested for H_2O .



Fig. 9. Newly precipitated euhedral crystals of ammonium perchlorate in initially dewetted sample after reheating at 72°C and 20 mm of vacuum

Because it is necessary for a sample to be exposed to moisture before it will embrittle, and exposure to moisture apparently results in solution of the salt at the interface, it might be suggested that embrittlement is due to increased reinforcement of the binder by ammonium perchlorate which has been precipitated by the low temperatures. However, low-temperature storage at -32°C of both a dewetted but dried (over CaSO_4) sample and a damp, dewetted sample did not produce any visible changes in either sample.

3. Ammonium Sulfate

After 18 days at 100% RH, ammonium sulfate displayed a partial dewetting around the margins of the

Table 3. Relative solubilities of fillers in POPG 2025, 20°C

Filler	Solubility, %
Lithium perchlorate	>2
Ammonium perchlorate	0.35
Potassium perchlorate	—
Potassium chloride ^a	<0.005

^aMoisture content of POPG, 0.05%.

sample, with complete dewetting at the extreme edges. There was no dewetting at all at 76% RH, even after 39 days. Because Aerojet conditioned their samples at 80% RH, this may explain why they did not observe embrittlement in ammonium sulfate-loaded samples. Rehealing of the partially dewetted grains occurred after 36 hr at 72°C and 29 in. Hg, resulting in whiskers of crystals growing on the original grains. There was no migration and precipitation within the binder.

This observation also suggests that migration with subsequent precipitation throughout the binder is a necessary prerequisite of embrittlement. Lithium perchlorate, the most mobile and soluble of all the salts studied, also embrittles the most intensely.

4. Glass Beads

The beads showed no changes in appearance after 21 days at 100% RH. The surface imperfections visible on the dry beads could not be seen at any time.

IV. ELECTRICAL PROPERTIES

A. Experimental

Qualitative electrical measurements were selected to verify vacuole formation occurring in mechanical dewetting and especially in moisture-induced dewetting, as was observed under the microscope. Also, such measurements should furnish evidence of solution and migration of the ammonium perchlorate in a propellant system. It was reasoned that capacitance should increase upon vacuole formation and resistance should decrease upon saturation of a binder or propellant sample with an electrolytic solution. Unfortunately, it was possible to measure the capacitance of only the mechanically dewetted sample; the sample dewetted by moisture diffusion conducted a current and capacitance measurements were not possible on our apparatus. However, this fault was a virtue when measuring resistance. The resistance in ohms was measured along the maximum dimension of a propellant sample $0.5 \times 1.0 \times 0.25$ in. Binder samples $1.0 \times 1.0 \times 0.25$ in. were measured in the same manner. These binder samples were then immersed for 2 months under saturated solutions of ammonium sulfate, ammonium perchlorate, and lithium perchlorate and subsequently measured again.

B. Results

The capacitance of three disk-shaped propellant samples, 2.0 in. in diameter and 0.05 in. thick, averaged 11.8 picofarads at 100 kc. After mechanical dewetting, the average was 18.1 picofarads; such an increase—greater than 50% in this case—could be attributed to the greater dielectric constant of a porous sample containing many air or vacuum spaces.

The results of resistance measurements are outlined in Table 4.

Table 4. Change of resistance of propellant samples with respect to environmental changes

Environment	Resistance, Ω	
	Pure binder	Propellant
Immediately after cure	$>10^9$	$>10^9$
60 days at 100% RH	$>10^9$	—
60 days over CaSO_4 desiccant	$>10^9$	—
24 hours at 100% RH	—	2.50×10^5
Sample above dried over CaSO_4 for 24 hours	—	$>10^9$
60 days immersed in saturated solution of LiClO_4	2.65×10^5	—
60 days immersed in saturated solution of $\text{NH}_4\text{ClO}_4^a$	1.75×10^5	—
60 days immersed in saturated solution of $\text{NH}_4(\text{SO}_4)_2$	$>10^9$	—
^a Physical appearance was sticky, soft, and definitely degraded in some manner; material had started to go into solution.		

As can be seen from the table, the ammonium perchlorate and the lithium perchlorate-loaded systems apparently go into solution and migrate when exposed to high relative humidities. Precipitation of crystals within the binder that had been immersed in saturated salt solutions was not observed after drying over CaSO_4 , but vacuum oven drying may have produced this as was earlier observed microscopically. Diffusion of moisture into the propellant also produced changes in resistance interpreted as an indication of complete saturation with the conducting salt solution resulting from solution of the filler. Judging from microscopic observations, this solution takes place at the interface, consequently damaging the binder-salt adhesive bond.

V. DIFFUSION RATE

Because of the detrimental effect that water has on the physical properties and storage characteristics of ammonium perchlorate-polyurethane solid propellant, it is necessary to determine the diffusion rate of moisture into such a system. An initial diffusion rate experiment was accomplished by filling flat-bottomed glass tubes to various depths with binder or propellant. A small piece of indicator paper, made by treating filter paper with cobaltous chloride solution and then drying, was placed in the bottom of each tube before the samples were cast. After curing, the samples were exposed to appropriate relative humidities at 23°C.

The indicator paper, as prepared for the experiment, changes color from bright blue to pale pink upon sorbing approximately 4.0×10^{-3} g H_2O/cm^2 . This takes approximately 25 to 30 min at room temperature and 100% RH. The indicator thus was not sensitive enough to give more than a qualitative measure of diffusion rates.

Figure 10 shows a qualitative value for the relative permeabilities of X500 binder and the same binder loaded with 60 wt. % of ammonium perchlorate. The rate of penetration of moisture through the binder proved to be greater than that through the propellant, at least for the rather large amounts required to affect the indicator. This could be caused by vacuole formation around the grains, which would act as sinks, or it could be caused by physical blocking of moisture penetration through the binder by the relatively impermeable ammonium perchlorate.

The presence of sinks is indicated by the equilibrium moisture content of the propellant, which is approximately 2.4 wt. % greater than the combined hygroscopicity of pure binder and ammonium perchlorate, taken separately. Physical blocking, on the other hand, has been shown to reduce the permeability of gases in filled rubbers (Ref. 6) and in polyethylene of varying degrees of crystallivity (Ref. 7). In the latter case the crystallites served as the filler.

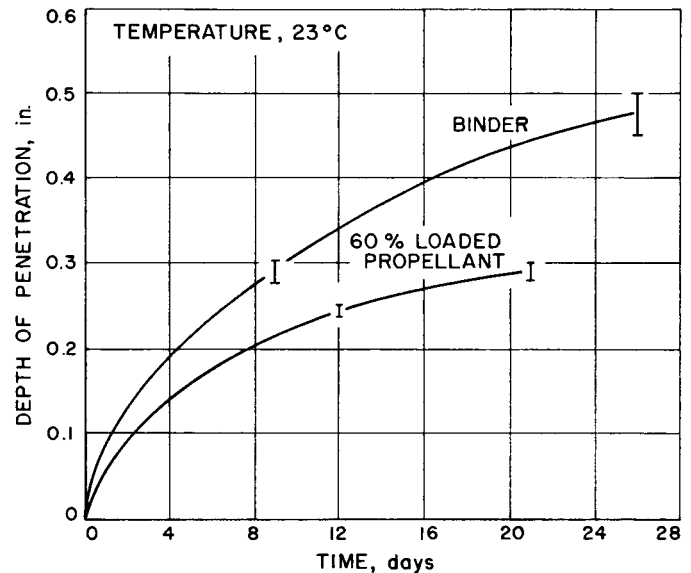


Fig. 10. Penetration of water through JPL X500 binder and 60% ammonium perchlorate-loaded propellant

VI. SORPTION OF H₂O AND D₂O

The sorption of water by propellant and binder appears to be largely physical, a combination of saturation of the binder and adsorption at the surface of the filler grain. The adsorption cannot be monomolecular, since far more water is picked up than can be accounted for by such a simple mechanism.

The amount of moisture sorbed and the binder-filler bond could be influenced by hydrogen bonding. Therefore, comparative weight-gain experiments were made by exposing the binder, the fillers, and the propellant to H₂O and D₂O. In all but one case, the mass of D₂O sorbed, after adjustment for its greater molecular weight, is slightly less than the mass of H₂O sorbed. This is

attributed to the lesser vapor pressure of the D₂O. The one exception was the ammonium perchlorate which sorbed D₂O at a five-fold greater rate than it sorbed H₂O. It is not yet known whether the equilibrium moisture content will differ by this factor. In any event, the final results of an investigation of this sorption behavior will be published later.

Although ammonium perchlorate sorbs D₂O at a greater rate than it sorbs H₂O, this does not appear to change the deleterious effects on the tensile properties of AP-loaded propellant. The stress-strain curves of tensile bars exposed to H₂O and D₂O for one week (100% RH in both cases) were identical.

VII. INFRARED SPECTROSCOPY

In searching for the mechanism of embrittlement, Aerojet considered phase changes, recrystallization, and the particle size or surface-to-volume ratio of the filler particles as well as crystallization and changes in the crosslink density of the binder. However, none of these could adequately explain the observed changes in the mechanical properties of propellant. Furthermore, previous studies at JPL showed that the mechanical properties of pure binder were unaffected by exposure to high relative humidities; the binder had to be loaded with a filler, and even then the properties were better than 90% reversible upon drying (Ref. 1 and 2).

Thus, there is little evidence for a chemical change as the origin or a major contributory cause of this phenomenon. In fact, the reversibility of the tensile property change argues strongly against such an effect. Nevertheless, during the current study, a color change was noted in the pure binder, and in the binder less than 1% loaded. This color change occurred in the samples no matter what filler was used—lithium perchlorate, ammonium sulfate,

or glass beads. Specifically, the binder studied was originally a rich amber color due to the iron acetylacetonate catalyst. After 2 weeks of storage at 100% RH at room temperature, the samples were bleached to a lemon yellow at their exposed surfaces. This color change was irreversible upon drying over P₂O₅ for 28 days or even in a vacuum oven at 65°C for 30 hrs. By visible spectrum analysis, other workers have found this color change to be due to the disappearance of the FeAA peaks. Moreover, the FeAA catalyst in an ammonium perchlorate system apparently does not remain evenly distributed through the binder during cure. Instead, it seems to migrate and concentrate around each perchlorate grain, because the binder developed a speckled effect resembling the measles. This effect was not observed with any of the other fillers. The congregation of the FeAA on the surface and around the AP grains may explain why a much greater catalyst-to-resin ratio must be used in propellant than in pure binder; the removal of FeAA from the binder interstices may leave behind an inadequate concentration unless the ratio is increased.

Concomitant color and chemical changes ordinarily suggest spectroscopy as a useful investigative tool, but the transmission of propellant samples is too low for the technique to be useful. However, a reflectance technique has recently been developed (Ref. 8) permitting studies even on opaque samples.

In this technique, called attenuated total reflection (ATR), a sample is placed in contact with the face of a prism of a material with a higher refractive index. A light beam can be reflected from this prism-sample interface because of the difference in refractive indices. However, the refractive index of the sample changes greatly in the region of an absorption band, producing a correspondingly large change in the angle of reflection. Thus part of the incident beam is reflected out of the detection path and the observed intensity falls off resulting in a beam attenuated in the same frequency regions found for transmission spectra.

However, recent work comparing the results of ATR and conventional transmission infrared spectroscopy has shown discrepancies between the two methods. For example, amplitudes of peaks are in some cases greatly changed. But more important, it was shown that there was a significant shift of frequency response of some bonds. Therefore, the results reported here are considered to be qualitative rather than quantitative.

The reflectance unit⁴ was used with a KRA-5 prism at a 40 deg incidence angle. The spectrometer was an Infracord 137.

A. Experimental

Samples of pure binder and of binder loaded with 60 wt. % of unground ammonium perchlorate were prepared and cast into special molds designed for the purpose. An 80% loaded propellant sample was milled to the correct size from a larger block. Pure ammonium perchlorate was prepared as a 1% KBr pellet, and its spectra was obtained by standard transmission techniques. A spectrum was run on the binder immediately after cure, after 19 days at 100% RH, and finally after drying over CaSO_4 for 13 days. The 60% loaded binder was measured dry, after 6 days at 100% RH, and finally after drying at room temperature over CaSO_4 for 7 days.

⁴ATR-1, Connecticut Instrument Corp., Wilton, Conn.

B. Results: Binder

As can be seen in Fig. 11 a, b, and c, there were no changes in the spectra except for the appearance and disappearance of the hydroxyl peak in the $3\text{-}\mu$ regions.

C. Results: Propellant

1. Dry Initial Propellant

Figure 12a is the spectrum of the 60% ammonium perchlorate-loaded propellant, immediately after cure. Comparison of this spectrum with Fig. 11a (pure binder, immediately after cure) shows no significant difference. Furthermore, none of the ammonium perchlorate bands that appear in Fig. 12d are obvious in the propellant spectrum. From this, it may be assumed that the propellant spectrum is due to the binder only, with no absorption by the AP. It is not known whether this surface-layer binder can be assumed to be equivalent to the interfacial material between perchlorate grains.

2. Wet Propellant

Figure 12b is the spectrum of 60% ammonium perchlorate-loaded propellant after 6 days at 100% RH. All response peaks are shifted down-frequency slightly from their position in the initially dry propellant, probably an apparatus variation. The peak appearing at $4.35\text{ }\mu$ is probably CO_2 . Its appearance and disappearance can be attributed to differences in path length between the sample and reference beams and variable attenuation of the reference beam.

The cause of a peak of $6.25\text{ }\mu$ in the wet propellant, which subsequently disappears upon drying, has not been determined at this time. Two other new peaks appear in the wet propellant at 3.2 and 7.1 to $7.3\text{ }\mu$ after drying (Figs. 12 b and c). The peak at $3.2\text{ }\mu$ is interpreted to be a combination of OH and NH_4^+ .

Apparently, ammonium perchlorate sufficient to respond to the infrared goes into solution in the binder during exposure to H_2O , and either remains in solution or precipitates out in microscopic and submicroscopic crystals during drying. A spectrum run on dry 80% propellant (Fig. 13) also shows the presence of these two bands at 3.15 and $7.15\text{ }\mu$. This would support the idea that the peaks appear only when the ammonium ion concentration in the binder is sufficiently high; e.g., higher than was present in the initial dry 60% loaded propellant

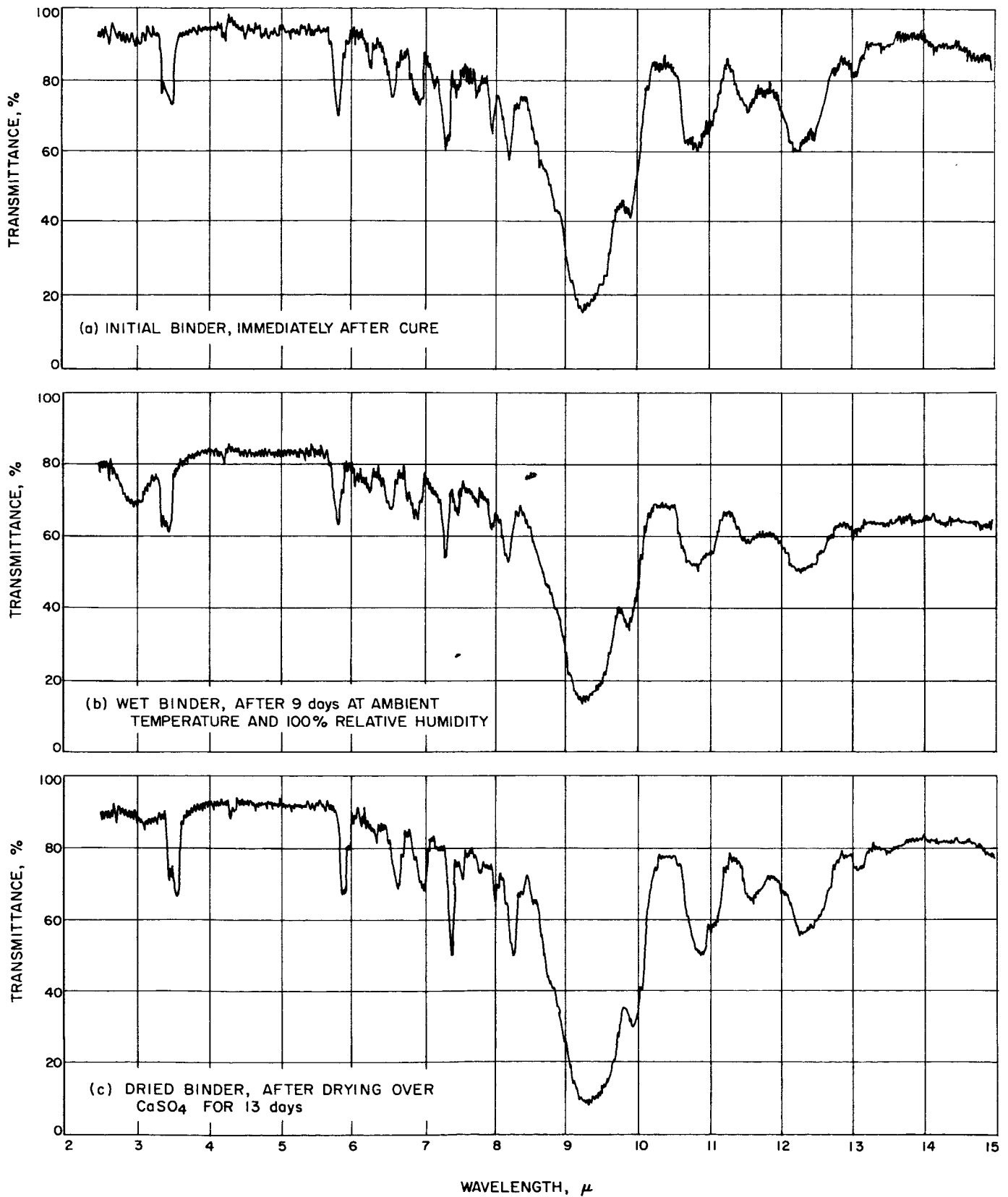


Fig. 11. Reflection infrared spectrum of X500 binder

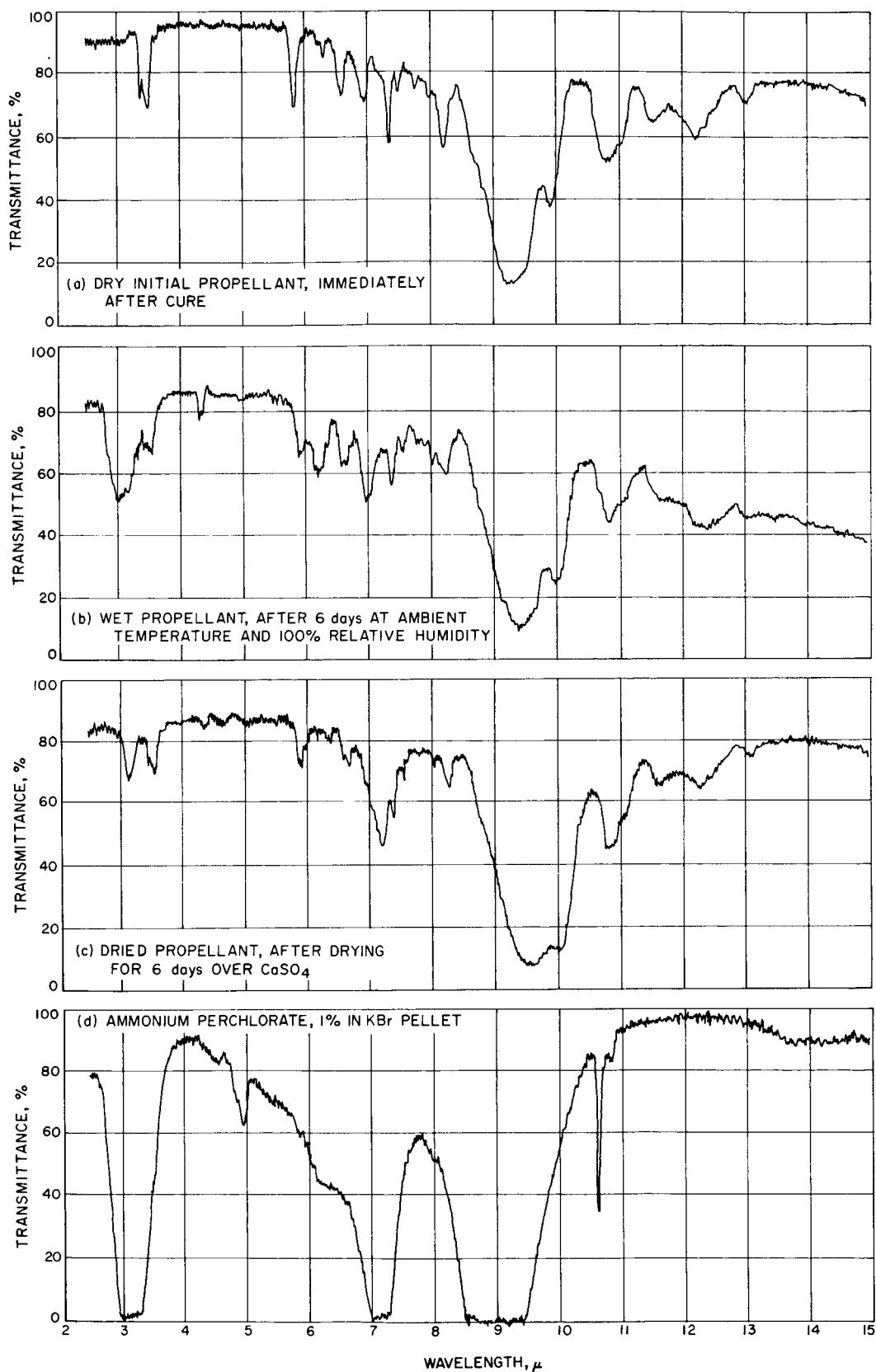


Fig. 12. Infrared spectrum of 60% ammonium perchlorate-loaded propellant

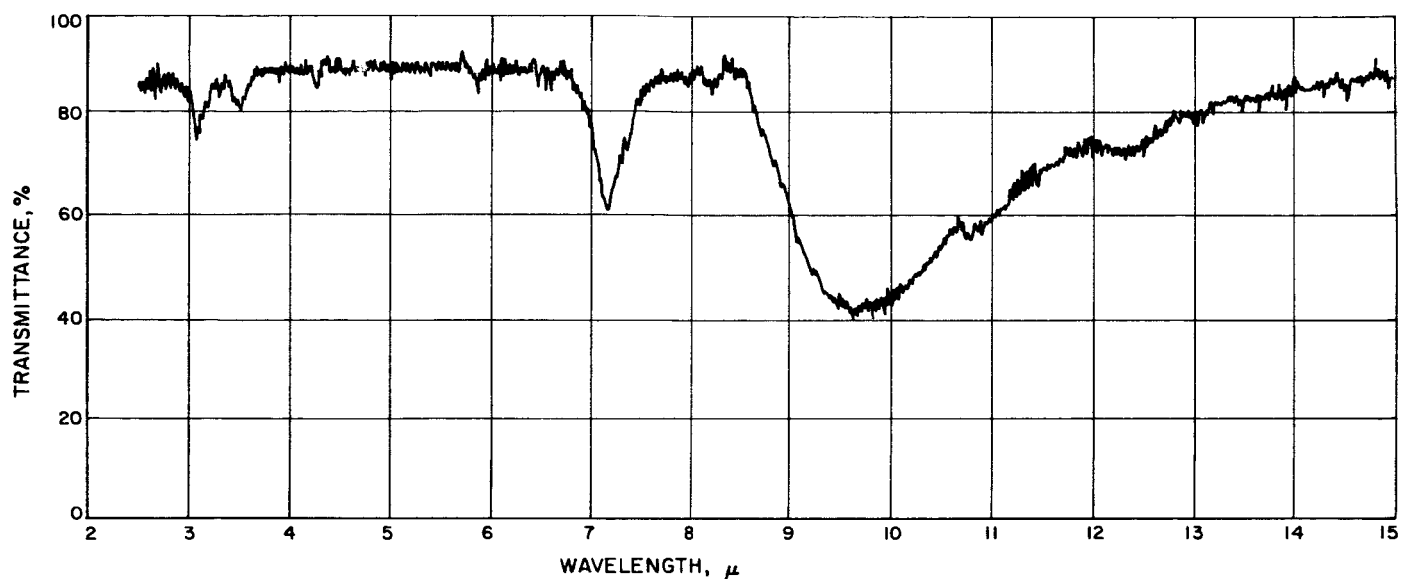


Fig. 13. Infrared spectrum of 80% bimodal ammonium perchlorate-loaded propellant

of Fig. 11a. Milling of the 80% sample would expose AP at the surface, while the cast 60% sample would have a surface layer of binder. Since the maximum depth of

penetration of the light beam of the ATR apparatus may be less than the depth of the binder layer, the quantitative comparison of the two experiments may be misleading.

VIII. SUMMARY

Ammonium perchlorate-filled propellant appears to be physically separated from the binder when exposed to relative humidities greater than 15% at ambient temperatures. Apparently, at high temperatures, this process is reversible by thorough drying of the sample. The mechanism of reversal seems to be a healing of the salt-binder adhesion on the surface of the initial grains and additional reinforcement provided by the precipitation of new, euhedral crystals of ammonium perchlorate.

The small-strain dynamic shear compliance instability with time is established to be a function of the previous humidity history and the environment at the time of measurement. The direction of drift and absolute value of the modulus is only indirectly a function of previous thermal history. There appears to be an optimum amount of water necessary for maximum embrittlement at any given temperature and additional water tends to decrease embrittlement.

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